MARKES international

TDTS

Thermal Desorption Technical Support

Note 68: Using Markes emission screening technology to simplify compliance with the latest construction product regulations

Keywords

Construction Products Regulation, Construction Products Directive, EC Mandate M/366

Introduction

Regulatory requirements relating to construction products and the indoor environment are currently undergoing major review in many parts of the world. Key examples are:

- European Commission (EC) mandate M/366 of the Construction Product Directive (CPD) and the new EC Construction Products Regulation (CPR)
- US International Green Construction Code (IgCC)
- European and Chinese regulations on hazardous chemicals ('REACH')
- 2009 French law describing the labelling of construction and decorative products

With the population of the EU now exceeding 500 million, the impending implementation of the EC CPR will have arguably the biggest impact on construction and decorative product trades around the world. When finalised, the CPR will require manufacturers to carry out chemical emissions testing as part of the CE marking process. Both product certification by an accredited third party laboratory and routine, in-house 'factory production control' of emissions are expected to be required.

Reference methods for emissions testing are specified for product certification. They are designed to simulate real-world use of the product after installation in a building and are, by definition, time-consuming (3–28 days) and expensive to run. To complement reference methods, quicker, simpler emissions screening tests have been introduced for routine industrial applications. New technologies/procedures allow chemical emissions screening to be readily implemented in a routine factory production (quality) control environment. This will reduce the test burden on industry and aid the development of low-emission, higher-value products.

With innovations such as the Micro-Chamber/Thermal Extractor™ (µ-CTE™) for fast emissions screening and TargetView™ for automatic interpretation of complex gas chromatography/mass spectrometry (GC/MS) data, Markes International has been at the forefront of efforts to simplify material emissions testing for manufacturers. This Markes publication summarises recent regulatory changes, the likely impact on industry, and ongoing technical developments to minimise the burden and maximise the opportunity for affected trades.

Changes in the regulatory landscape

Since 1989, Essential Requirement (ER) 3 of the EC Construction Products Directive has stated that chemical emissions from products used indoors must not adversely affect the indoor environment or the health and comfort of building occupants. A wide range of structural and decorative materials are covered by this legislation; however ER3 was not properly implemented for many years, largely due to the lack of suitable and broadly applicable ('horizontal') test methods.

Current legislative activity is rectifying this situation; in 2005, EC mandate M/366 was adopted under the CPD and required the European standards organisation (CEN) to finalise and validate methods for testing chemical emissions. A new CEN Technical Committee (TC 351) was set up to complete the task, with the aim of making chemical emissions testing a mandatory part of CE marking for construction products across Europe. This process is now well underway and has been reinforced by the promulgation of new German and French national regulations, which require emissions testing and establish performance criteria for product approval or classification.

In parallel with the ongoing work of CEN TC 351, European legislators have been developing a replacement to the 1989 Directive. The new Construction

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Products Regulation (CPR) is currently progressing through the final stages of debate in the European Parliament and is expected to be adopted by the end of 2010, with implementation by 2012. 'Regulations' differ from 'Directives' in Brussels' terminology in that they enter European law immediately; *i.e.* without member states having to pass their own national regulation.

The EC REACH ('registration, evaluation, authorisation and restriction of chemical substances') directive, relating to chemicals and their safe use, was adopted by the European Parliament and came into force in June 2007. Similar legislation is currently being implemented in China. Under REACH, chemical manufacturers, importers ***and downstream users*** will need to prepare technical dossiers and/or 'Chemical Safety Reports' depending on tonnages. If a consumer product contains a potentially hazardous chemical at a level above 0.1%, and if it is possible for that chemical to be emitted under normal usage conditions (intentional or unintentional release), this must be assessed. Current guidance on implementation of emission testing for *articles and preparations* (general consumer goods) under European REACH specifies many of the methods developed for construction products [1].

Concern relating to product emissions and their potential impact on indoor environments and human health are driving similar regulatory developments in the US. A consortium of American agencies including the national standards agency ANSI and the indoor air quality interest group ASHRAE have recently produced Standard 189.1 (2009) '*Standard for the design of high-performance green buildings*'. In parallel with this, another US agency, the International Code Council, is collaborating with ASTM and the American Institute of Architects to incorporate mandatory emissions testing into US building codes for public building projects. This '*International Green Construction Code*' (IgCC) initiative is expected to be fully implemented and enforced by 2012.

Which industrial sectors (trades) will be affected?

Amendments to construction product regulations impact a surprising number of trades, including those involved in the manufacture of thermal insulating materials, wood-based products, plasterboard, paints and varnishes, adhesives, sealants for joints, flooring materials, structural foam and wall coverings.

In the long term, REACH-type regulations around the world are expected to expand the requirement to monitor chemical emissions away from just construction materials, to include a wide range of consumer products used indoors. Theoretically, over 70% of manufacturing industry could be impacted.

What do reference methods for materials emissions testing involve?

Standard reference methods for testing product emissions to indoor air involve placing a representative sample of the material into a large test chamber to simulate real-world use. The chamber is then connected to a supply of clean air. The chamber exhaust is sampled and analysed for chemicals at various times. The methods are usually broken down into multiple sections covering sample collection and preparation, emissions testing and vapour analysis.

The most important 'horizontal' reference methods for emissions testing have been developed by the International Organization for Standardization (ISO) and are now available as parts 6, 9, 10 and 11 of ISO standard 16000. ASTM standards D5116, D5197, D6196 and D7143 are also important. CEN TC 351 is in the process of amalgamating and validating ISO 16000 series standards under mandate M/366 of the CPD. Once this work is completed, chemical emissions testing, *per* TC 351-validated methods, will become a mandatory part of CE marking for construction products, first under the CPD and subsequently under the CPR.

Reference methods for emissions testing typically include guidance on the following:

- How to collect and prepare samples of materials/product to test.
- What sort of emissions test chamber equipment to use and what conditions to apply (loading, temperature, humidity, air flow, *etc.*).
- When to collect and measure the emissions (typically after 3, 12 and/or 28 days).
- How to collect and analyse the chemicals emitted by the sample, and how to use the results to calculate product emission levels. Two main approaches are used for this:
    1. (S)VOC analysis: Sampling onto sorbent tubes with subsequent thermal desorption (TD) and GC/MS analysis for volatile and semi-volatile organic compounds (VOCs and SVOCs).
    2. Formaldehyde: Sampling onto DNPH cartridges with subsequent liquid chromatography (HPLC) analysis.

Some construction products generate very complex (S)VOC emission profiles comprising multiple individual compounds. An example GC/MS data set is shown in Figure 1.

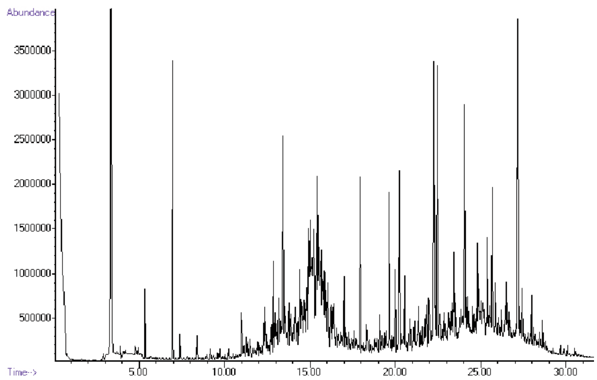

Figure 1: Complex chemical emission profile from a flooring product analysed by TD-GC/MS

Product approvals and labelling schemes

Before a reference method can be implemented by an accredited laboratory, it must be adopted into a product approval protocol. Certification protocols specify the test method plus additional requirements, such as when it should be carried out, which compounds to target and, most importantly, pass/fail criteria (*i.e.* limit levels for emissions).

Key national emissions test protocols include the German AgBB scheme, the French AFFSET scheme, the Finnish M1 label and the Californian specification 01350. There are also many voluntary, sector-specific emissions labelling schemes like the GUT carpet label or EMICODE for adhesives. A schematic of the AgBB approval process is shown in Figure 2 as an example. The AgBB scheme, AFFSET protocol and 01350 specification include extensive and regularly updated lists of 150 or more target chemicals plus class 1 and 2 carcinogens.

Harmonising the large number of protocols used today is extremely challenging due to the history and vested interests of the proponents of each individual label; however, harmonisation is crucial to the success of CE marking. It is also essential for ensuring manufacturers are not required to carry out multiple similar tests on the same products to get the broad approval they need for global distribution.

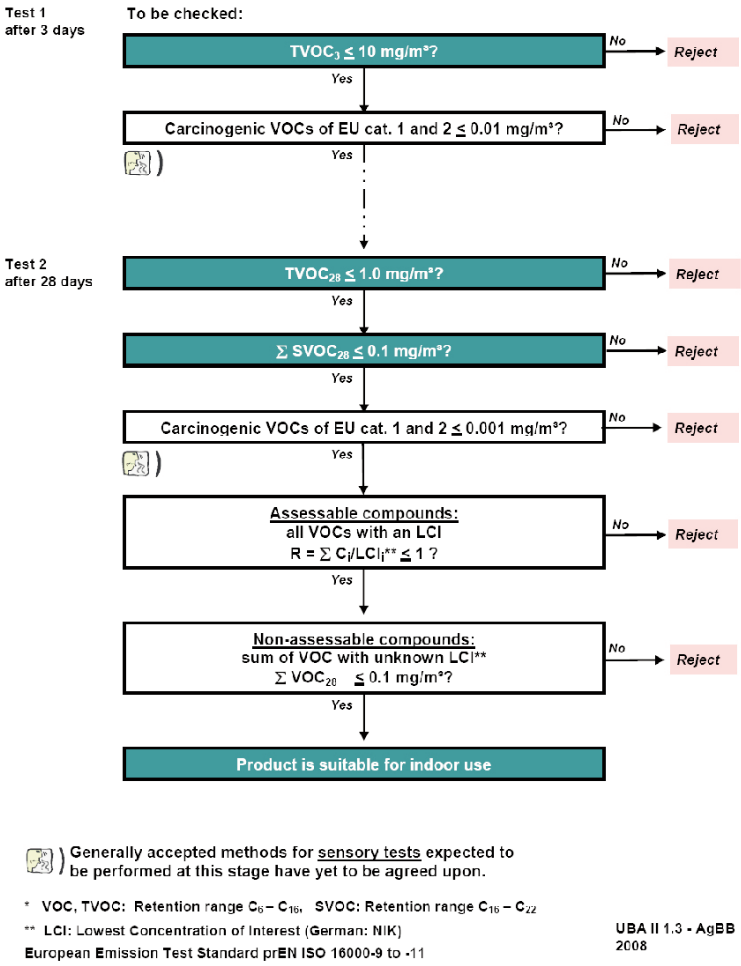

Figure 2: Flow chart for the evaluation of VOC and SVOC emissions from building products under the German AgBB scheme

There are a number of European and international initiatives currently working on harmonisation of product approval criteria, most notably an EC expert group under the umbrella of the Joint European Research Centre at Ispra in Italy. By the time the CPR is adopted and standard validation work within CEN TC 351 is completed, it is expected that a harmonised product approval process will be available for CE marking and that it will follow the general principles of the German AgBB, the French AFFSET protocol and the Californian 01350 specification. It is further expected that, in Europe, relevant product-related technical committees within CEN will be heavily involved in setting specific performance (pass/fail) criteria for their types of product.

Once the core criteria for incorporating emissions testing into CE marking have been finalised, it is further expected that some of the most important voluntary labels will sit alongside the CE mark to provide optional additional information/product-differentiation.

Fast emissions screening for 'factory production control'

Reference methods are preferred for formal product certification because they generate analytical data that relates most closely to real-world use. However, even from the brief description above, it is clear that these methods are time-consuming and complex, *i.e.* they are expensive for manufacturers. The time required (several days, even weeks) also precludes the use of these standard procedures for quality control of production or for convenient testing of prototype materials under development. Thus, while there are few that would contest the use of these reference methods for formal product certification, there is an additional need for a complementary rapid and cost-effective emissions screening method that could be carried out by manufacturers.

The need for an 'initial' or 'screening' method to complement the formal certification test methods is highlighted in EC Mandate M/366 of the Construction Product Directive. Once adopted, the CPR will also drive significant demand for quick, secondary emissions screening as it will stipulate both certification of chemical emissions by an accredited third party laboratory (using reference methods) plus routine *factory production control*. US regulations, such as the California Air Resources Board (CARB) Formaldehyde Rule, also require producers to monitor conformity with emission levels on a routine basis.

Historically, screening methods for VOCs have either involved GC/MS analysis of the 'volatile' content of products applied as liquids (*e.g.* ISO 11890-2 for measuring the organic content of paint) or direct thermal desorption with GC/MS analysis of small solid or liquid samples (see Figures 3 and 4). However, it can be difficult to correlate such VOC 'content' data with results from reference emissions tests. Manufacturers of paint or paint additives, for example, can design products that contain solvent, but in which the solvent is encapsulated such that it can never escape to the indoor environment. Content testing is also generally unsuitable as a guide to emissions from composite products, *e.g.* laminated materials.

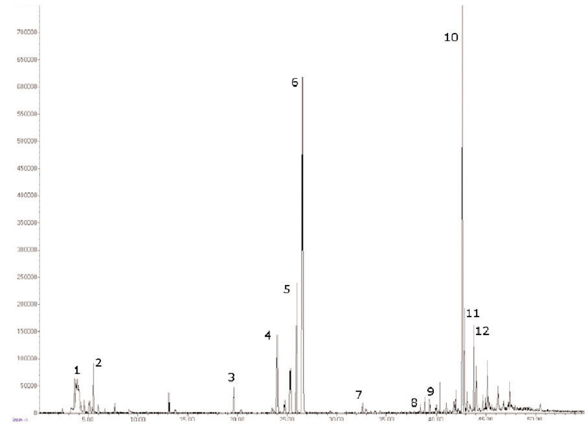

Figure 3: Artificial leather analysed for VOC content using direct TD with GC/MS

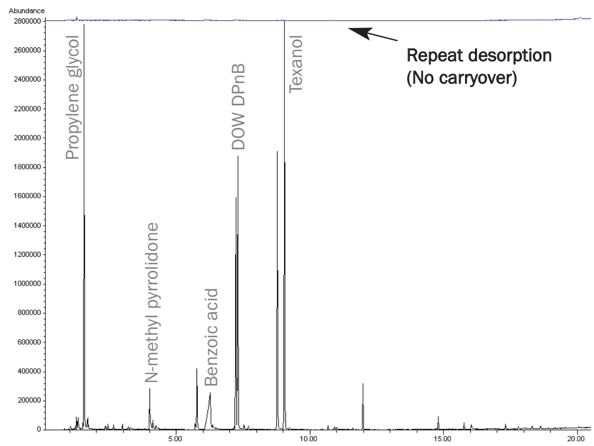

Figure 4: Analysing the solvent content of water-based paint using direct TD with GC/MS

Micro-chamber technology was pioneered by Markes International to address industry's need for a fast emissions screening method that correlates with reference tests. 'Micro-chambers' are scaled-down versions of the larger chambers; they are based on the same fundamental principles and can be used for surface-only or bulk emissions testing, but are typically operated at slightly elevated temperatures (30–65ºC) to speed up equilibration. Micro-chamber data produced within 30–40 minutes of sample preparation provide a reliable indicator of longer term emissions test results for many products [2, 3], thus making it an ideal tool for rapid emissions screening. Relevant industrial applications include:

- Factory production control of emissions (quality control)
- In-house checks on emission profiles across a product range; different colours, finishes, etc.
- R&D of low emission products
- Monitoring the quality of raw materials
- Comparison with competitive products
- Micro-chamber methods for emission screening are currently under development by leading standards agencies to complement longer-term reference tests. Key examples are listed [4–7].

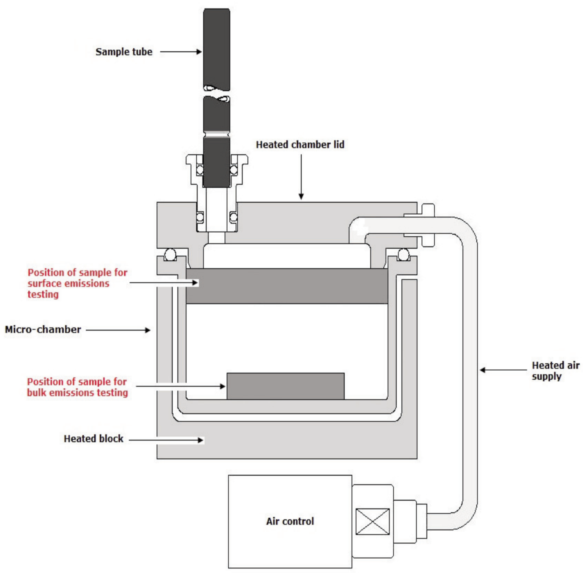

Figure 5: Schematic of the Markes micro-chamber

Micro-Chamber/Thermal Extractor (µ-CTE) technology from Markes International

Markes µ-CTE technology is available in two rugged and portable configurations which are both suitable for use in industrial laboratories. The smaller unit comprises six 44.5 mL chambers (45 mm I.D. x 28 mm depth; represented in Figure 5) and operates at a maximum temperature of 120°C (M-CTE120). The larger unit houses four 114 mL chambers (64 mm I.D. x 36 mm depth) and operates at a maximum temperature of 250°C (M-CTE250; Figure 6). The chambers themselves are available in polished stainless steel, or can be inert (Silco)-coated for compatibility with reactive chemicals (*e.g.* odorous compounds). User-selectable parameters include equilibration time, sampling time, temperature and gas flow rate.

Figure 6: Micro-Chamber/Thermal Extractor (M-CTE250) from Markes International

The µ-CTE is easy to use and requires minimal sample preparation. Circular samples are typically punched or cut out of planar materials and placed into separate chambers, such that the upper (emitting) surface is raised up to the circular baffle (collar) projecting down from the chamber lid. This eliminates interference from edge and rear surface emissions. Irregular materials (such as polymer beads or moulded components) are simply placed or weighed into individual chambers, and liquid or resinous materials are prepared on suitable substrates in the normal way. The temperature of the micro-chamber is typically set above ambient (30–65ºC) to speed up equilibration and optimise sensitivity without significantly changing the emission profile. Proprietary technology [8] controls a constant flow of clean, dry gas or air to each chamber, allowing four or six samples to be tested simultaneously. The flow remains constant whether or not vapour sampling devices (sorbent tubes or DNPH cartridges) are connected to the chamber outlets. No pumps or electronic mass flow control equipment are required, which makes the system very easy to use. Typical gas/air flow rates are 50 mL/min for VOC analysis or 250 mL/min for formaldehyde. The vapour sampling devices are subsequently analysed by TD-GC/MS or HPLC, respectively, in the normal way.

Once samples have been introduced to the micro-chamber pots they are then placed into a µ-CTE unit at the prescribed temperature, the lids are closed and the gas/air supply turned on. The samples are then left to equilibrate for 20–30 minutes (longer if semi-volatiles are of interest). Vapour sampling tubes are connected to the outlet of each chamber at the end of the equilibration period, and VOCs are typically collected for 15 minutes. This allows VOC emissions to be tested from four or six samples per hour, depending on which µ-CTE unit is used. Testing formaldehyde or SVOC emissions may take slightly longer, depending on emission rates and the range of compounds of interest. Markes' four chamber µ-CTE can also be used for SVOC emission testing according to ISO 16000-25 [9].

As an example, the VOC emissions from a sample of plasterboard tested using the µ-CTE, followed by TD–GC/MS, is shown in Figure 7.

A more detailed description of µ-CTE operation and performance is presented in the Markes International publication TDTS 67.

Simplifying data interpretation and analysis

An additional way in which emissions screening can be simplified, particularly for less experienced industrial laboratories, is to deskill the interpretation of the complex emission profiles. ALMSCO International (a division of Markes) has developed an innovative new software tool, TargetView™, to automatically detect multiple target compounds in complex TD-GC/MS data sets, even if the compounds of interest are at trace levels (Figure 8). This new software aids comparison with control levels, thus simplifying rapid and reliable pass/fail assessment.

Figure 8 shows the plasterboard emission data seen in Figure 7 with the application of TargetView to automatically identify target components present. Target compounds and unknown compounds are represented by red bars, the height of which gives an indication of peak area. The software harnesses two separate powerful mathematical algorithms to deconvolute and analyse the mass spectral data to automatically detect target compounds. Data processing takes about a minute per file (see TDTS 89 for more information). When complete, TargetView produces a simple report for the sample, listing every detected target compound and the associated degree of confidence (Figure 9).

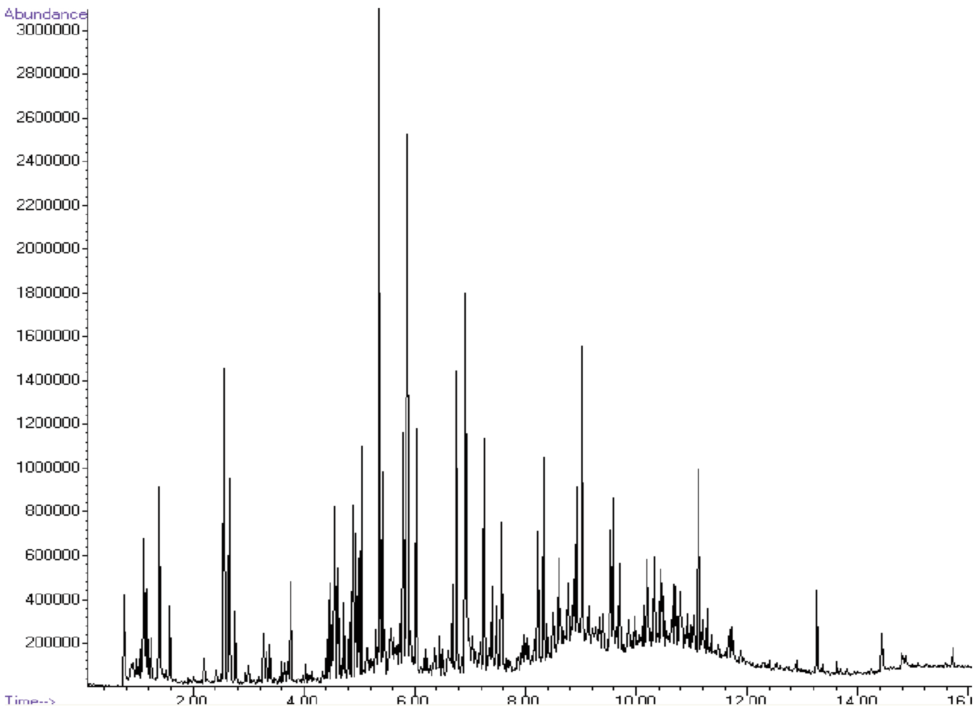

Figure 7: Chemical emission profile from a plasterboard product using the µ-CTE with TD-GC/MS analysis

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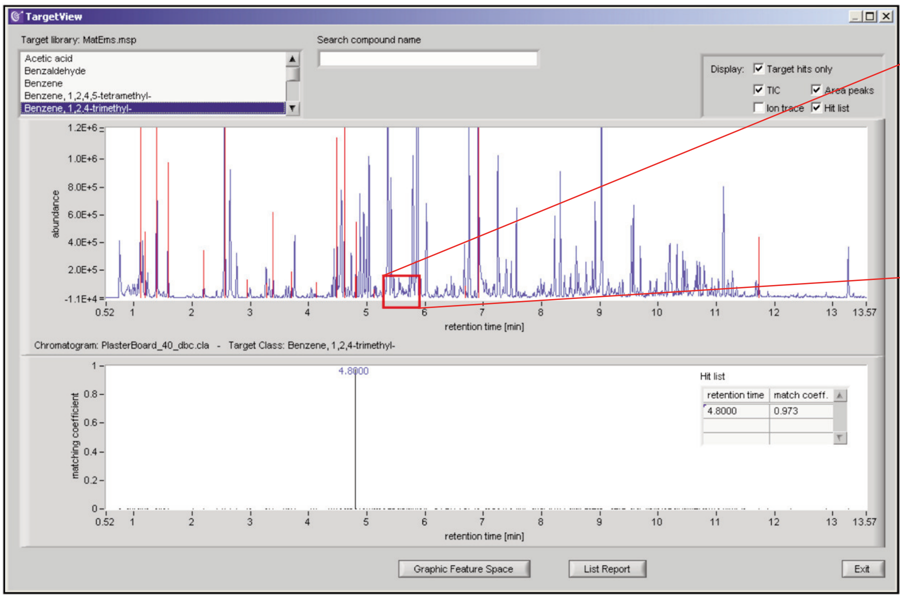


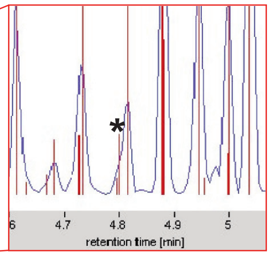
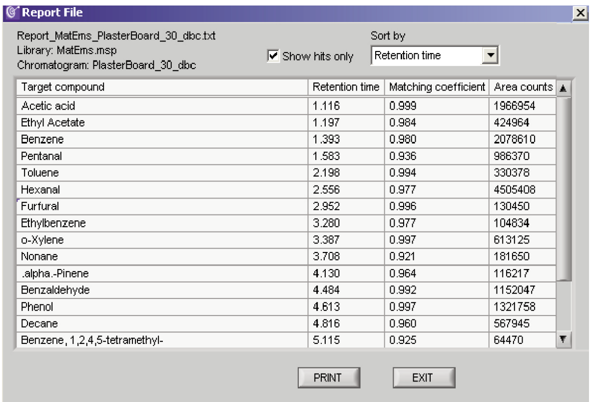


Figure 8b. Enlarged view of highlighted area showing the target compound trimethyl benzene (*) co-eluting with multiple compounds in a small peak

Figure 8a: TargetView interface. Upper pane - Plasterboard emission profile (as Figure 7) with automatic detection of target peaks (red bars). Lower pane - Detection of trimethyl benzene and corresponding match coefficient.



Target compound	Retention time	Matching coefficient	Area counts
Acetic acid	1.116	0.999	1966954
Ethyl Acetate	1.197	0.984	424964
Benzene	1.393	0.980	2078610
Pentanal	1.583	0.936	986370
Toluene	2.198	0.994	330378
Hexanal	2.556	0.977	4505408
Furfural	2.952	0.996	130450
Ethylbenzene	3.280	0.977	104834
o-Xylene	3.387	0.997	613125
Nonane	3.708	0.921	181650
.alpha.-Pinene	4.130	0.964	116217
Benzaldehyde	4.484	0.992	1152047
Phenol	4.613	0.997	1321758
Decane	4.816	0.960	567945
Benzene, 1,2,4,5-tetramethyl-	5.115	0.925	64470

Figure 9: Automated post-run report displaying target hits

Comparison of automatic data analysis by TargetView *versus* lengthy, manual data interpretation by a GC/MS expert has confirmed that TargetView processing is at least as reliable.

As TargetView leaves original data files intact and unaffected, these can be used for TVOC calculations. No information is lost or compromised by TargetView.

Conclusion

Manufacturers need to be aware of, but not alarmed by, current regulatory developments in the construction products sector and how these changes could impact their business. As well as third party certification of products, the requirement for factory production control of product emissions means that most companies will want to implement some sort of emissions testing in-house. Markes has focused considerable development efforts on producing technology such as the µ-CTE sampling unit and TargetView software, which can be used for rapid screening of product emissions while maintaining data quality and correlation with reference emissions methods in compliance with regulatory requirements.

These innovations will not only minimise the burden of routine quality control of emissions, but will also allow manufacturers to assess emission levels from prototype products in R&D. This will ultimately speed up development of new, higher-value 'green' product ranges, thus protecting consumers and giving the company a competitive edge over manufacturers of cheaper, high-emission imports.

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